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(54) ELECTRICAL CABLE, PREFERABLY HIGH-VOLTAGE CABLE

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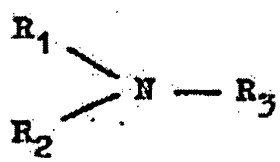
Electrical Cable, Preferably High-Voltage Cable
Addendum to the patent … … (Patent Application P 21 39 599.3)

The object of the main patent … … (Patent Application P 21 39 599.3) is an electrical cable, preferably a high-voltage cable, whose insulation consists of an olefin polymer, in particular of a polymer or copolymer based on ethylene. According to the invention of the main patent, the cable insulation contains a small addition of aliphatic, aromatic or mixed aliphatic-aromatic saturated tertiary mono-, di-, or polyamines, whose substituents are pure hydrocarbons. According to the invention, a saturated tertiary amine is used, which does not contain any additional heteroatoms besides tertiary amino nitrogen; instead, the entire molecular structure only contains pure hydrocarbon groups as well as tertiary amines. The saturated mono-, di-, or polyamines, which are provided in the main patent as additives, thus have the following structure:



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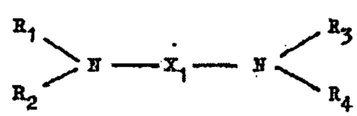

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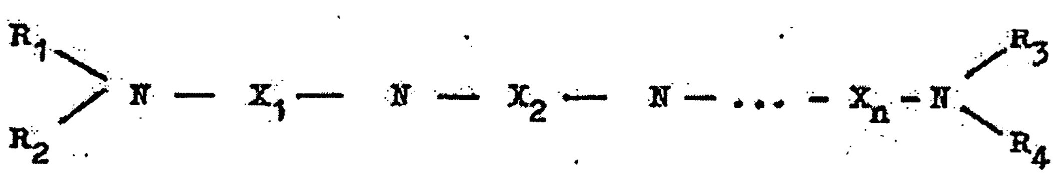
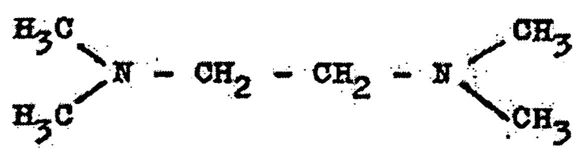


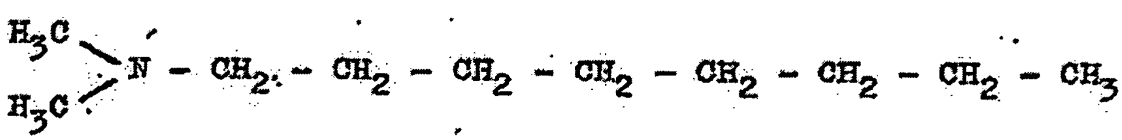
Here the substituents R_1-R_4 as well as X_1-X_n are alkyl, aryl, cycloalkyl or cycloaryl groups, that is aliphatic, aromatic, cycloaliphatic or cycloaromatic groups; these groups can also be mixed aliphatic-aromatic. They can be identical to each other or different from each other. The only essential factor is that they are pure hydrocarbons which thus contain no heteroatoms.

In the main patent, the following have already been indicated as examples of suitable compounds:



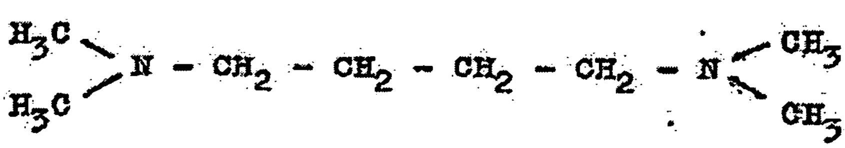
(N,N,N',N'-tetramethylethylenediamine)

or



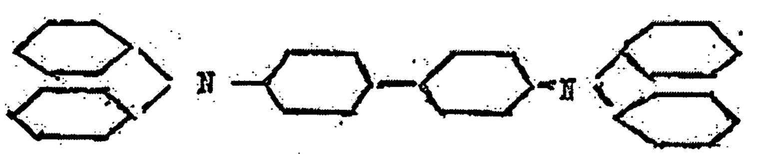
(N,N-dimethyloctylamine)

or



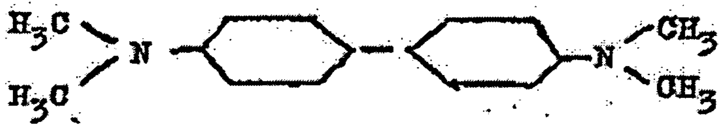
(N,N,N',N'-tetramethyldiaminebutane)

or



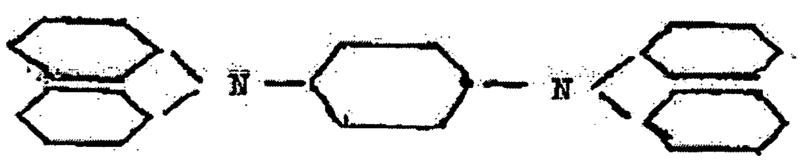
(N,N,N',N'-tetraphenylbenzidine)

or



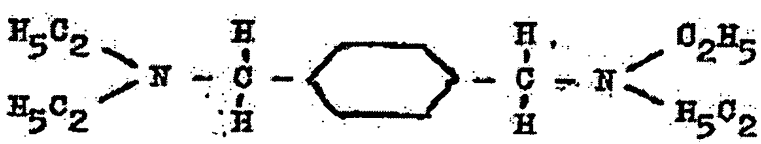
(N,N,N',N'-tetramethylbenzidine)

or



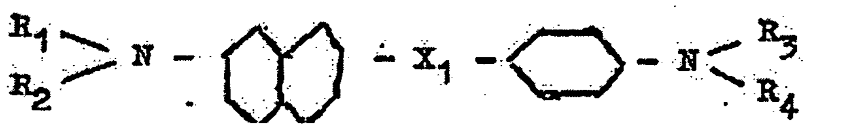
(N,N,N',N'-tetraphenyl-p-phenylenediamine)

or



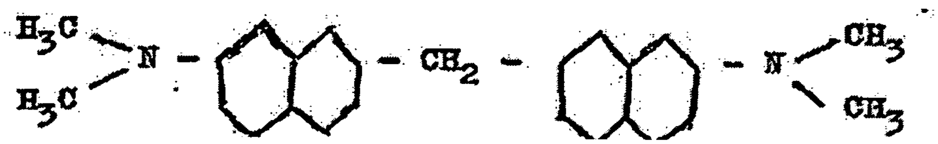
(N,N,N',N'-tetraethyl-p-xylene-α,α'-diamine)

or



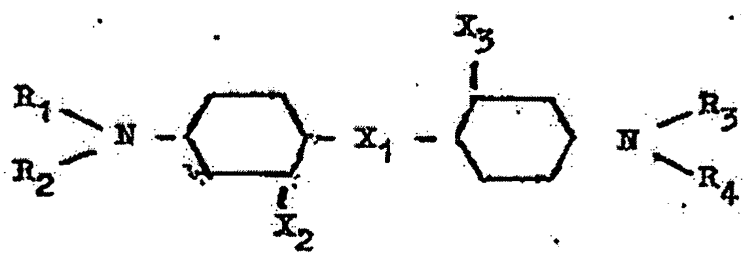
(tetra-substituted naphthylenephenylenediaminoalkane)

or

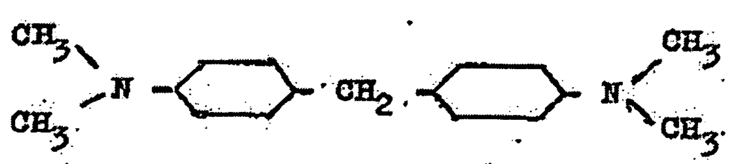


(N,N,N',N'-tetramethyldinaphthyldiaminomethane)

However, the aromatic groups can also be substituted with additional pure hydrocarbon groups. This leads to saturated tertiary amines having, for example, the following structure:



As already indicated in the main patent, it has been shown that saturated tertiary amines having the structure of a tetraalkyldiaminodiarylalkane are suitable, for example, N,N,N',N'-tetraethyl-p-xylene-α,α'-diamine or also N,N,N',N'-tetramethyldiaminodiphenylmethane. The last mentioned compound, which thus has the structure



has been shown to be extraordinarily advantageous.

The invention is based on the problem of further improving an insulation for an electrical cable, preferably a high-voltage cable, which has been designed according to the main patent, where the improvement concerns the electrical properties and also the resistance to aging.

To solve this problem, the invention provides for adding to the insulation of a cable designed according to the main patent--which contains saturated mono-, di-, or polyamines--as additional additives, high-boiling-point, highly aromatic oils based on hydrocarbons, and having an aromatic compound content of at least 40%, in a quantity of 2-10 wt%, preferably 2-5 wt%. Thus, it is essential for the invention that, together with the addition of saturated tertiary mono-, di-, or polyamines, which has already been provided for according to the main patent, high-boiling-point, highly aromatic oils based on hydrocarbon with a relatively high aromatic compound content are also added. This combined addition of the two mentioned components results in an increase in the resistance to voltage stresses as well as an increase in the resistance to aging.

It is advantageous for the additives of the insulation to be added in a quantity that is compatible with the olefin polymer, if possible after allowing the additives to sweat.

In itself, it is already known to add oil-like additives to cable insulations constructed on the basis of a polyolefin (DT-OS 1 569 396, DT-OS 1 949 539). In the case of the mentioned insulation mixtures based on polyethylene, as a rule the goal is, however, to introduce, through the oil-containing components, solid substances into the insulation, in other words, the oily components are used in a manner of speaking as a "vehicle oil." In contrast, the purpose of the invention is to add to the insulation according to the main patent--which already contains effective saturated tertiary mono-, di- or polyamines—additionally high-boiling-point, highly aromatic oils based on hydrocarbons, which further increase the resistance to voltage of the insulation due to a synergistic effect.

To carry out the idea of the invention, it is recommended to choose, as the boiling range for the high-boiling-point, highly aromatic oils that are used as an additional additive, a range of approximately 140-300°C, preferably 160-250°C ,at 5 Pascal.

Furthermore, it has been shown to be advantageous to choose the high-boiling-point, highly aromatic oil that is used as an additional additive in such a manner that the components of

paraffins, isoparaffins, naphthenes, an and aromatic compounds in the fractions of this oil, which are produced during distillation, correspond at least qualitatively to the components of paraffins, isoparaffins, naphthenes, and aromatic compounds of this oil [sic; appears to be redundant]. In other words, this means that the crucial factor in choosing the high-boiling-point, highly aromatic oil used to carry out the concept of the invention is that the individual proportions of this oil during fractional distillation do not, for example, evaporate one after the other; instead, that the composition of the oil in the fractions produced during distillation are at least qualitatively preserved. Smaller quantitative deviations do not interfere here. Thus, for example, the aromatic compound proportion in the higher-boiling-point fractions can increase by a small amount, quantitatively speaking.

Furthermore, it has been shown to be advantageous if the high-boiling-point, highly aromatic oils that are used as additional additives present a relatively low specific resistance of approximately 10^{10} to 10^{15} $\Omega{\cdot}cm$; in other words they must present a relatively high intrinsic conductivity. In addition, the tan δ value – that is, the loss factor – should be as high as possible.

For carrying out the concept of the invention, high-boiling-point, highly aromatic petroleum or mineral oil fractions that are liquid at room temperature, and that have a content of aromatic compounds and naphthenes of approximately 40-70 wt%, preferably 50-60 wt%, and a nonaromatic residue what is aliphatic or cycloaliphatic, have been shown to be suitable for carrying out the concept of the invention. The condensed aromatic compounds contained in such petroleum fractions, as well as in mineral oil fractions obtained from coal tar, have an advantageous effect on the voltage stabilization. It has been shown that it is particularly advantageous to use petroleum or mineral oil fractions, if their specific resistance is relatively low, for example, approximately 10^{10}-10^{11} $\Omega{\cdot}cm$. The tan δ value of the oils used, measured at 20°C, 50 Hz, and 2.5 kV/mm, should be at least 10^{-1}, preferably 1.0-1.5 or more.

Furthermore, it is recommended to ensure that the high-boiling-point, highly aromatic petroleum or mineral oil fractions do not contain peroxides or form peroxides during a longer period of time with aging at approximately 80°C. Indeed, the latter condition prevents a destruction of the antioxidants contained in the olefin polymer of the insulation, so that a good resistance to aging of the insulation is guaranteed.

Furthermore, it is advantageous for the high-boiling-point, highly aromatic petroleum or mineral oil fractions to contain organically bound heteroatoms, in particular sulfur, in a quantity

of at least 1 wt%, preferably 3-4 wt%. For example, sulfur can be contained in the form of thiophene derivatives in the petroleum or mineral oil fraction.

Examples of petroleum or mineral oil fractions that fulfill the above listed condition, for carrying out the concept of the invention, are petroleum or mineral oil fractions that are marketed, for example, under the names Dealen D 18 from the company Deutsche Texaco AG., Hamburg, Polymerol 6028 from the company Deutsche Shell AG., Frankfurt/Main, or Dutrex 298 from the company Shell Oil Comp., USA.

As already mentioned, one adds to the cable insulation based on an olefin polymer--in particular a polymer or copolymer of ethylene--the high-boiling-point, highly aromatic petroleum or mineral oil fractions in a quantity of 2-10 wt%, preferably 2-5 wt%. The saturated tertiary mono-, di-, or polyamines are here advantageously added in a quantity of 0.1-2 wt%, preferably 0.5-0.8 wt%, with reference to the total proportion in the insulation. The special effect, which is the result of the combined use of the high-boiling-point, highly aromatic petroleum or mineral oil fractions as well as the saturated tertiary amine already provided in the main patent, is based on a synergistic effect. The voltage stabilizing effect of the amines, which in itself is already known, is increased by the also voltage-stabilizing addition of the oil fraction, so that the total increase in the voltage stabilization is greater than that which would be achieved by the addition of the two individual proportions, each alone.

For carrying out the concept of the invention, it is, however, also possible to use--as additional additives—high-boiling-point, highly aromatic synthetic oils based on hydrocarbons, which are liquid at room temperature. It has been shown to be particularly advantageous to use here synthetic oils whose molecules contain at least two benzene rings that are interconnected via a carbon atom.

In itself, the addition of such aromatic hydrocarbons is known from DT-PS 1 490 574. However, for the invention it is essential that one jointly use such aromatic hydrocarbons and the saturated tertiary mono-, di-, or polyamines, which have already been mentioned in the main patent, as the additive to an insulation based on an olefin polymer, in particular a polymer or copolymer of ethylene.

To carry out the invention, it has been shown to be particularly advantageous to use a mixture of substitution isomers of dibenzyltoluene. Advantageously, the aromatic compound

content of the substitution [substituted] isomer mixture of dibenzyltoluene is greater than 50 wt%, preferably up to 80 wt%.

While the proportion of the high-boiling-point, highly aromatic synthetic oils, that is, for example, the proportion of the above-mentioned substitution isomer mixture of dibenzyltoluene, is chosen to be approximately 2-10 wt%, preferably 2-5 wt%, with respect to the [total proportion of] insulation, it is recommended to choose the proportion of the simultaneously used saturated tertiary amines in a quantity of 0.1-2 wt%, preferably 0.5-0.8 wt%, with reference to the total proportion in the insulation. In the same manner as with the petroleum or mineral oil fractions mentioned in the introduction, one then obtains a synergistic effect with regard to increase in the voltage stabilization by the addition of the high-boiling-point, highly aromatic synthetic oil and the saturated tertiary amine.

With regard to the boiling range of the synthetic oil used, as well as the composition of the fractions produced in the fractional distillation, it is recommended to use the same conditions as indicated earlier for the petroleum or mineral oil fractions.

High-boiling-point, highly aromatic synthetic oils based on hydrocarbons, such as, a mixture of substitution isomers of dibenzyltoluene, themselves have a relatively strong tendency to form a hydroperoxide or diaryl peroxide. This tendency to form peroxides, as well as the peroxide content, which in practice always is found in a synthetic oil, such as, in an isomer mixture of dibenzyltoluene, in themselves entail a risk that the effectiveness of the agent for protection against aging, which is added to the olefin polymer, in particular to polyethylene, will be so strongly reduced that the resistance to aging of a cable insulation that has been constructed in this manner would be jeopardized. However, it has been shown that the joint addition of saturated tertiary amines has an inhibitory effect on peroxides. Thus, a good aging behavior is guaranteed for such a cable insulation based on an olefin polymer, in particular polyethylene, for the service life of the cable, which is of extraordinary importance for medium-and high-voltage cables.

Compounds that in themselves are organic, and have functional groups, have been proposed, such as, compounds with sulfur compounds of the thioether, thioester disulfide, or sulfoxide type, as well as phosphorous compounds such as, the esters of phosphoric acid and derivatives of thiophosphoric acids. However, it has been shown that, for example, an isomer mixture of dibenzyltoluene-soluble disulfides, thioesters, and sulfoxides has no peroxide-inhibiting effect. The same applies to phosphites of different esters of phosphoric acid, which

only partially present a slight peroxide-inhibiting effect. In addition, the last mentioned phosphites present a tendency to hydrolyze with the formation of phosphoric acid, so that their use for cable insulation mixtures based on polyethylene is not possible in view of the required long-term resistance.

In contrast to the above, the amines that have already been mentioned in the main patent, and having the structure of a tetraalkyl-diamino-diaryl alkane--when high-boiling-point, highly aromatic synthetic oils based on hydrocarbons have been added,--present an extraordinarily strong peroxide-inhibiting effect, particularly if the addition is made to a substitution isomer mixture of dibenzyltoluene. This applies in particular for N,N,N',N'-tetramethyldiaminodiphenylmethane, which has already been mentioned in the main patent.

This saturated tertiary amine not only protects against hydroxide formation, but it also degrades the hydroperoxide present in the mixture. As a result, a chain reaction is prevented, in which one mole of diaryl peroxide and one mole of water are formed from two moles of hydroperoxide, which would have an unfavorable effect on insulation for medium-or high-voltage cables.

In a variant of the main patent, it is therefore also possible to add--besides the high-boiling-point, highly aromatic oils based on hydrocarbons, which are used as additional additives--the saturated tertiary amines in only a quantity that promotes peroxide inhibition, namely a quantity of less than 0.1%. Such a small addition of a saturated tertiary amine, for which one can consider using, in particular a tetraalkyldiaminodiarylalkane, more particularly tetramethyldiaminodiphenylmethane, can be used for all those application purposes of a cable with an insulation based on an olefin polymer where a sufficient increase in the voltage stabilization is achieved by the addition of the high-boiling-point, highly aromatic oil. This applies both to synthetic oils and to petroleum or mineral oil fractions.

To explain the invention, two embodiment examples of cable insulation mixtures are indicated below.

<u>Example 1:</u>

95.6% of a high-pressure polyethylene, to which 0.05% of a phenol-based antioxidant are added, is mixed with 4% of a high-boiling-point, highly aromatic petroleum fraction, which is liquid at room temperature and which presents a relatively high intrinsic conductance as well as a

high tan δ value and an aromatic compound content of approximately 50%, as marketed by the company Texaco under the commercial name "Dealen D 18," along with 0.4% tetramethyldiaminodiphenylmethane.

Example 2:

96.6% of a high-pressure polyethylene, to which 0.05% of a phenol-based antioxidant are added, are mixed with 3% of an isomer mixture of dibenzyltoluene and 0.4% tetramethyldiaminodiphenylmethane.

The following table gives an overview of the advantages achieved using a cable insulation mixture based on a high-pressure polyethylene and which contains 0.08% diphenyl-p-phenylenediamine as an antioxidant and constructed according to the invention, and, for comparison, an insulation mixture constructed according to DT-OS 1 569 396 or DT-OS 1 949 539. 97.6% of this high pressure polyethylene mixed with 2.0% CD 101, 0.2% diphenylamine, and 0.2% 2,4-dinitrotoluene. CD 101 is a highly aromatic oil manufactured by the Boron Oil Company, Cleveland, Ohio, and which presents a specific weight of 1.045, a solidification point of -6.7°C, a viscosity of 21 cSt at 38°C and 3 cSt at 99°C, a refractive index of 1.601, and an aniline point below 15°C. This insulation mixture is called insulation mixture according to the state of the art in the following table.

In the following tables, an overview of the short-term resistance and the long-term resistance in unscreened model cables. The short-term resistance here is determined by an immediate perforation test (alternating current) and the long-term rigidity is determined in a test conducted in a pellet bath (approximately 15 kV/mm). The indicated percentages for the probability of failure are determined according to Weibull for the short-term resistance and according to Gauss for the long-term resistance.

Because of the different origins of the high-pressure polyethylene used in each case, the indications provide the values for the mixture as well as the values for the PE [polyethylene] base, including each antioxidant.

The wall thickness of the unscreened model cables used for the measurement tests was 1.0 mm in the immediate breakdown test and 1.5 mm for the pellet bath test.

Table 1.
Short-term resistance in kV/mm

Failure probability	Known insulation mixture		Insulation mixture according to Example 1		Insulation mixture according to Example 2	
	PE base	Mixture	PE base	Mixture	PE base	Mixture
50%	53	63	48	91	48	88
70%	56	68	50	100	50	92
95%	62	78	53	115	53	100

Table 2. Short-term resistance in min

Failure probability	Known insulation mixture		Insulation mixture according to Example 1		Insulation mixture according to Example 2	
	PE base	Mixture	PE base	Mixture	PE base	Mixture
50%	295	1200	220	3000	220	1800
70%	360	1600	260	4300	260	3000
95%	510	1800	350	7100	350	4200

0 Figure
17 Claims

Claims

1. Electrical cable, preferably a high-voltage cable, whose insulation consists of an olefin polymer, in particular a polymer or copolymer based on ethylene, where the cable insulation contains a small addition of aliphatic, aromatic or mixed aliphatic-aromatic, saturated tertiary mono-, di-, or polyamines, whose substituents are pure hydrocarbons, according to Patent ... ... (Patent Application P 21 39 599.3 – VPA 71/4721), characterized in that the insulation, which contains saturated tertiary mono-, di-, or polyamines, has additional additives of high-boiling-point, highly aromatic oils based on hydrocarbons with an aromatic compound content of at least 40% in a quantity of 2-10 wt%, preferably 2-5 wt%.

2. Electrical cable according to Claim 1, characterized in that the additional additives are added to the insulation in a quantity that is compatible with the olefin polymer.

3. Electrical cable according to Claim 1, characterized in that the melting point range of the high-boiling-point, highly aromatic oils that have been used as additional additives is approximately 140-300°C, preferably 160-250°C, at 5 torr.

4. Electrical cable according to Claim 3, characterized in that the components of paraffins, isoparaffins, naphthenes and aromatic compounds in the fractions present during distillation of the high-boiling-point and highly aromatic oil that has been used as an additional additive correspond at least qualitatively to the components of paraffins, isoparaffins, naphthenes, and aromatic compounds [sic].

5. Electrical cable according to Claim 1, characterized in that the high-boiling-point, highly aromatic oils, which are used as additional additives, have a relatively low specific resistance of approximately 10^{10} to 10^{15} Ω·cm as well as a tan δ value that is as high as possible.

6. Electrical cable according to one or more of Claims 1-5, characterized in that the additional additives are high-boiling-point, highly aromatic petroleum or mineral oil fractions, which are liquid at room temperature, and present a content of aromatic compounds and naphthenes of approximately 40-70%, preferably 50-60%, whose nonaromatic residue is aliphatic or cycloaliphatic.

7. Electrical cable according to Claim 6, characterized in that the high-boiling-point, highly aromatic petroleum or mineral oil fractions neither contain peroxides nor form them over a longer period of time during aging at approximately 80°C.

8. Electrical cable according to Claim 6, characterized in that the high-boiling-point, highly aromatic petroleum or mineral oil fractions contain organically bound heteroatoms, in particular sulfur, in a quantity of at least 1%, preferably 3-4%.

9. Electrical cable according to one or more of Claims 1-4, characterized in that the additional additives are high-boiling-point, highly aromatic synthetic oils, which are liquid at room temperature, and based on hydrocarbons.

10. Electrical cable according to Claim 9, characterized in that each molecule of the synthetic oil contains at least two benzene rings that are bound to each other by a carbon atom.

11. Electrical cable according to Claim 10, characterized in that mixture of substitution isomers of dibenzyltoluene is used as the synthetic oil.

12. Electrical cable according to Claim 8, characterized in that the aromatic content of the used substitution isomer mixture of dibenzyltoluene is greater than 50%, preferably greater than 80%.

13. Electrical cable according to Claim 6 or 9, characterized in that the saturated tertiary mono-, di-, or polyamines are added in a quantity of 0.1-2%, preferably 0.5-0.8%, with respect to the total proportion in the insulation.

14. Electrical cable according to Claim 6 or 9, characterized in that, besides the high-boiling-point, highly aromatic oils based on hydrocarbons, which are used as additional additives, the saturated tertiary amines are only added in a quantity that promotes peroxide inhibition, namely a quantity of less than 0.1%.

15. Electrical cable according to Claim 14, characterized in that a tetraalkyldiaminodiarylalkane is used as the saturated tertiary amine.

16. Electrical cable according to Claim 15, characterized in that a tetramethyldiaminodiphenylmethane is used as the saturated tertiary amine.

17. Electrical cable according to one or more of Claims 1-16, characterized in that the cable insulation is a crosslinked polymer or copolymer of ethylene.

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